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GAS DIAGNOSTICS UTILIZING LASER INDUCED RAMAN SCATTERING

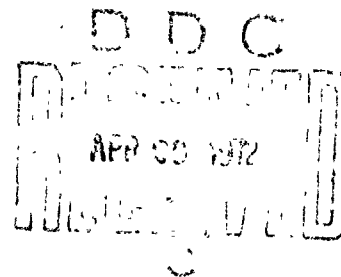
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**AEROSPACE RESEARCH LABORATORIES
AIR FORCE SYSTEMS COMMAND
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WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

FOREWORD

This report was prepared for the Aerospace Research Laboratories, Air Force Systems Command, United States Air Force, by Dr. Anthony A. Boiarski, Visiting Research Associate of The Ohio State University Research Foundation under Contract F33615-67-C-1758. The work reported herein was performed under Work Unit 23, "Gas Dynamics Research" of Project 7065, "Aerospace Simulation Techniques Research" under the technical cognizance of Mr. Fred L. Daum and the overall direction of Mr. Elmer G. Johnson.

· ABSTRACT

The feasibility of using various techniques to determine the chemical and thermodynamic state of individual species in a flowing gas mixture is discussed. It is theoretically shown that, utilizing the Raman scattering technique, species concentrations can be determined for individual molecular constituents. Also, the static temperature of the gas and the vibrational temperature of molecular species can be obtained. The apparatus used for the present Raman scattering measurements is described and experimental data on the species concentrations of oxygen and nitrogen in air are presented. Application of the Raman scattering technique will greatly enhance the amount of information which can be obtained from high enthalpy real gas flows around hypersonic vehicles, in rocket plumes as well as jet engine exhausts. Limitations of the technique are also pointed out.

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SECTION I

INTRODUCTION

The diagnostics of non-equilibrium reacting gas flows poses many experimental difficulties. One problem arises from the fact that probes, when inserted directly into the flow, disturb the fluid sufficiently to render the results inconclusive. Hence, it is desirable to use some sort of remote sensing device, foremost among which are optical, spectroscopic, interferometric and microwave techniques. It is generally accepted that the spectroscopic techniques are best suited for diagnostic work since the other techniques can only ascertain gross properties of the gas, while spectroscopic analysis includes the possibility of examining individual constituents of a general gas mixture. The spectroscopic techniques that have been proposed include emission, absorption, electron beam induced emission, resonance fluorescence, Rayleigh scattering, Thompson scattering, resonance Raman Effect (RRE), and regular Raman scattering. A brief discussion of the advantages and drawbacks of each method will be presented with emphasis on the general theory and application of the regular Raman effect.

SECTION II

SPECTROSCOPIC TECHNIQUES

1. EMISSION

Spectroscopic techniques can be grouped into the three general areas of emission, absorption, and light scattering. Emission spectroscopy, itself, is useful for determining the presence of a number of the species expected in a high temperature flow, but no quantitative information about the molecular species concentrations can be obtained due to the complicated nature of the excitation process and self-absorption within the region of interest. Also, in many cases of aerodynamic interest, the densities and static temperatures are sufficiently low that the gas will not radiate of its own volition. Electron beam-induced emission offers quantitative data for nitrogen in the low density flow regime, but the technique is invalid at densities greater

than those corresponding to approximately 0.5 mm-Hg at room temperature. Another induced emission technique is resonance fluorescence, where a gas is optically pumped by an intense light source tuned to a particular electronic-vibronic absorption frequency. As in the electron beam technique, the molecule radiates after a particular lifetime of the excited state has elapsed. During this lifetime, a collisional event can occur and collision quenching of the radiation will invalidate the measurements at other than low densities. Also, reabsorption of the fluorescent radiation can occur to complicate the interpretation of the measured intensity. In summary, induced fluorescent techniques are applicable for quantitative data at low densities for a restricted number of molecules, while spontaneous emission has no quantitative value. To obtain chemical and thermodynamic data at higher densities for a larger number of gases of interest, some other technique must be applied. In Refs 1 and 2, discussions of the electron beam and resonance fluorescence techniques are presented.

2. ABSORPTION

Absorption techniques are theoretically sound and have been applied successfully to high enthalpy flow field analysis. However, many problems exist when one attempts to apply the technique to a general gas mixture. At some low gas densities, the method cannot yield results due to the lack of absorbing particles and the inability to experimentally distinguish small intensity changes of a high intensity source. Also, no point measurement is possible unless traverses are made of the entire absorbing region and an Abel integration is performed to obtain point properties. This process assumes radially symmetric flow and is cumbersome as well as inaccurate under certain experimental conditions. However, the greatest drawback to the application of absorption spectroscopy is the fact that nitrogen, oxygen, hydrogen, and all other homonuclear molecules of interest have no absorption spectrum. Only heteronuclear and some vibrational modes of polyatomic molecules are infrared active. Also, many experimental difficulties arise when working in the infrared region of the spectrum where the presence of water vapor with its strong absorption characteristics can invalidate absorption measurements of other gases as discussed in Ref 2.

3. LIGHT SCATTERING

When a high intensity monochromatic light beam is focused at a point in a flow field, scattered light may be observed at any angle to the incident beam. By choosing the frequency of the incident light properly, several types of scattering phenomena can occur. At any incident light frequency one will obtain

scattered light at the same frequency. This is called Rayleigh scattering and can be used to determine total gas density, but no information about the concentrations of the various constituents or temperature data can be obtained. Thompson scattering is scattering from electrons and ions in a plasma and can be used to obtain charged particle number densities for certain flow conditions.

By choosing a frequency of the incident light beam within the region of electronic-vibronic absorption of a molecule, one can obtain radiation from that particular molecule which is several orders of magnitude more intense than under normal conditions. This is the so-called resonance Raman effect (RRE). The general theory of RRE is well developed, but when applied to the interpretation of individual experimental results, the theory meets with difficulties. Also, experimental problems of reabsorption, fluorescence, and photolysis, seriously hinder the usefulness of RRE as a diagnostic technique. Resonance Raman effect can be used to detect the presence of some species, but quantitative measurements of chemical constituents or gas temperatures are difficult to make with the resonance Raman technique.

SECTION III

RAMAN SCATTERING

By choosing the incident light frequency outside the molecular resonance region, the ordinary scattering phenomena are observed. Most of the incident radiation is scattered elastically by gas molecules resulting in Rayleigh scattering mentioned above. A few photons, however, undergo inelastic interactions producing scattered photons at frequencies different from the incident light. The resulting spectrum is unique to the specific scattering molecule. This is the so-called Raman scattering effect. The feasibility of using Raman scattering as a diagnostic tool in fluid mechanics research has been discussed and demonstrated by several authors.³⁻⁷ These investigations have shown that species concentrations can be determined for individual molecular and ionic constituents in a general gas mixture. Also, the static temperature of the gas and the vibrational temperature of molecular species can be obtained. Hence, all the chemical and thermodynamic properties of interest can be measured without disturbing the flow field.

In Raman scattering, the electron cloud surrounding a molecule is perturbed during a photon-molecule interaction. This perturbation results in a polarization of the charge surrounding the nuclei. The molecular polarization is a function of the electronic, vibrational, and rotational state of the molecule. Hence, the scattered radiation can have a frequency, not only of the perturbing value (i.e., Rayleigh scattering), but also weaker radiation at frequencies displayed at predictable frequency shifts from the incident frequency (i.e., Raman scattering). It must be understood that the molecule is not itself radiating any new photons. Rather, the incident photon at frequency ν_0 has undergone inelastic scattering and its frequency has been altered to $\nu_0 \pm \Delta\nu$ where $\Delta\nu$ is a function of the scattering molecule. Of course, the molecule will also gain or lose some energy from the interaction. However, this molecular energy is redistributed to the rest of the molecules in the system through collisional processes. Hence, no collision quenching of the radiation occurs for Raman scattering.

The relative intensity of various types of scattering phenomena is shown in Fig 1. Rotational Raman scattering about the Rayleigh line is the most intense followed by vibrational Raman scattering and rotational scattering within the vibrational bands. In vibrational Raman scattering, molecular transitions between vibrational energy states dictate the frequency shifts of the scattered photons. A Stokes photon is generated when the molecule undergoes a transition from the $v = 0$ to $v = 1$ state, where v is the vibrational quantum number. An anti-Stokes photon results from a $v = 1$ to $v = 0$ transition. Further transitions (i.e., $v = 1$ to $v = 2$, $v = 2$ to $v = 3$, etc.) are also possible. The ratio of the Stokes to anti-Stokes (i.e., 0,1/1,0) intensities or the Stokes 0,1/1,2 band ratio is a sensitive indication of the vibrational temperature of a gas. Figure 2 shows these band ratios as a function of vibrational temperature for oxygen. The absolute intensity measurement of Raman Stokes bands along with the determination of the vibrational temperature will yield the number density of any and all species of interest.

In rotational Raman scattering, rotational transitions result in frequency shifted scattered photons which are indicative of the rotational energy state of the scattering molecule. The rotational temperature of the gas is determined by examining the rotational Raman spectra of the major species of a general gas mixture. Figure 3 shows a theoretical calculation of the unresolved rotational spectra about the Rayleigh line for a pulsed nitrogen laser at 3371Å having a 1.0Å and 0.1Å line half-width. For purposes of illustration, only the intensities less than one are plotted. The calculations involve numerical integration of a convolution of the Rayleigh line shape and Raman rotational line profiles with the spectrometer apparatus function. Collision and doppler broadening of the Raman lines and the isotropic portion of the Rayleigh line are included. A Lorentzian line

shape is assumed in the calculations. These theoretical computations dramatically illustrate the problem of attempting to make measurements of weak Raman rotational radiation near the broadened wings of the intense Rayleigh line. From Fig 3 it can be seen that accurate measurement of rotational temperatures is impossible with a 1.0\AA half-width laser line since the Rayleigh wings constitute the majority of the total radiation. However, Fig 3 also shows that the rotational structure can be measured if a 0.1\AA half-width source is used. Curve fitting of theoretical rotational spectra obtained in this manner with experimentally determined spectra will yield the rotational temperature of the gas.

SECTION IV

EXPERIMENT

The experimental set-up used at the present time is shown schematically in Fig 4. The laser is an AVCO pulsed nitrogen model with a 10 nanosecond pulse half-width and a peak power of 0.1 megawatts at 100 pulses/sec. The beam cross-section is rectangular rather than circular and is focused by lens #1. A 0.5" long segment of the beam is imaged onto the slit of a spectrometer by lens #2. The spectrometer is a tandem arrangement of two 1/4-meter Jarrell-Ash scanning spectrometers which reduces scattered light to one part in 10^7 . The spectrally analyzed radiation is detected by an uncooled RCA 3850 Quantacon photomultiplier tube. This tube has a quantum efficiency of 30% in the region of the Raman Stokes radiation from the N_2 pulsed laser. The detected pulses plus the photomultiplier noise are amplified by a PAR pre-amp and then fed into a PAR box-car integrator. Gate times of 12 nsec on the integrator, which are synchronously timed with the laser trigger generator, favor recording of the laser induced signal rather than photomultiplier noise or background radiation. Hence, by sampling and averaging techniques, the box-car integrator can detect pulsed signals buried in noise. The output of the integrator is recorded on an X-Y plotter as the wavelength drive of the spectrometer is scanned through the region of interest.

SECTION V

EXPERIMENTAL RESULTS

Some early experimental vibrational band spectra using a setup similar to Fig 4, but with a smaller scattering volume, is shown in Fig 5. Both the oxygen and nitrogen Stokes vibrational bands are present. Note that Rayleigh scattered radiation from a spontaneous laser emission line is also present in Fig 5. This secondary radiation could be eliminated by filtering of the incident laser light. Some of the first Raman vibrational intensity versus pressure data taken at ARL are shown in Fig 6. Note the expected linearity of the N_2 Stokes intensity with air pressure.

SECTION VI

PROBLEMS

The largest drawback to the present application of the Raman scattering technique is the low intensity of the scattered light at low pressures. This low Raman scattering intensity requires that high power laser sources with high incident photon fluxes be used if time resolved measurements are desired. Scattering cross sections for atoms are extremely small and only Raman scattering data from molecules and molecular ions can be obtained with current experimental techniques. Hence, no atom concentrations can be presently obtained. The problems of rotational temperature determination have been discussed above. The N_2 pulsed laser in use at the present time has a 1Å half-width making it unsuitable for rotational scattering at low temperatures. However, this laser can be operated on Neon whereby it lases at 5401Å with a laser line width of 0.1Å. This half-width should provide adequate rotational structure measurement capabilities as shown in Figure 2.

SECTION VII

FUTURE PLANS

A continuing effort is being exerted to extend the technique to lower and lower pressures. Adjustments and maintenance to the laser increased the power by a factor of 5 bringing it up to the rated value. The scattering volume will also be increased. Hence, useful Raman vibrational scattering measurements at sub-atmospheric pressures are expected to be attainable. Also, a small quartz pebble-bed heater has been constructed to make Raman temperature measurements at atmospheric pressure and temperatures up to 900°K. It is further planned to apply the above experimental technique or some modified version to flow diagnostics in the AFFDL Reentry Nose Tip (RENT) leg of the 50-megawatt arc-heated facility, as well as the ARL/LF supersonic combustion facility at Wright-Patterson Air Force Base.

SECTION VIII

CONCLUSIONS

Absorption techniques in moderate to high density flows of heteronuclear molecules, electron beam induced emission in low density nitrogen flows, and Thompson scattering from charged particles in a plasma are remote diagnostic techniques which have been applied successfully in the past. However, the density restrictions and limits of species accessible for study are serious drawbacks of these spectroscopic techniques. The Raman scattering technique presently under investigation offers the experimenter a tool to examine the chemical and thermodynamic state of many gases of interest over a wide density range in a flow environment. With the present and expected future emphasis on increased laser power, the drawback of low Raman scattering intensity at low gas density can likely be overcome. Hence, the technique could bring about a revolution in high temperature flow field analysis.

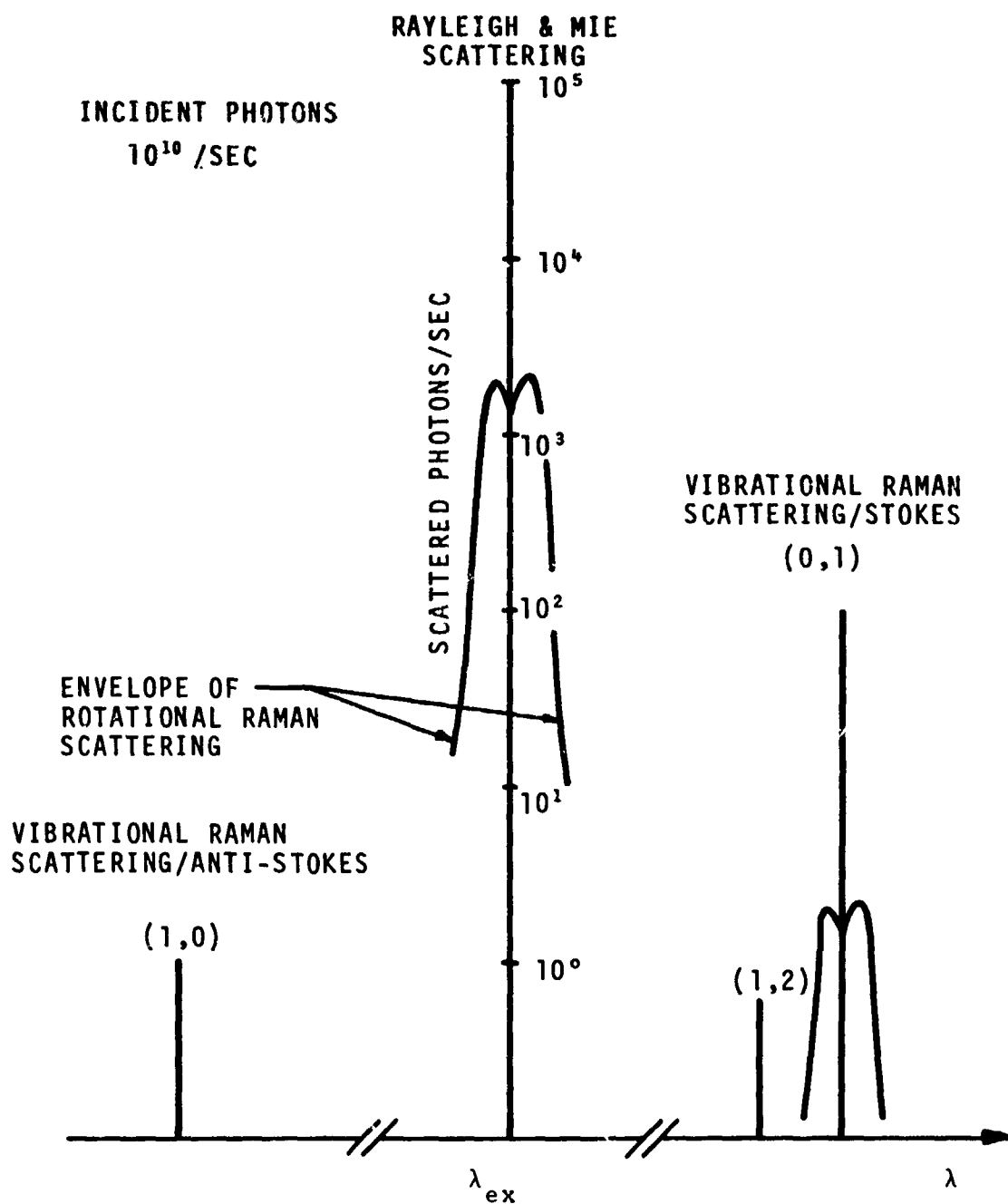


Figure 1. Relative Intensity of Various Types of Scattering Phenomena at Low Temperature

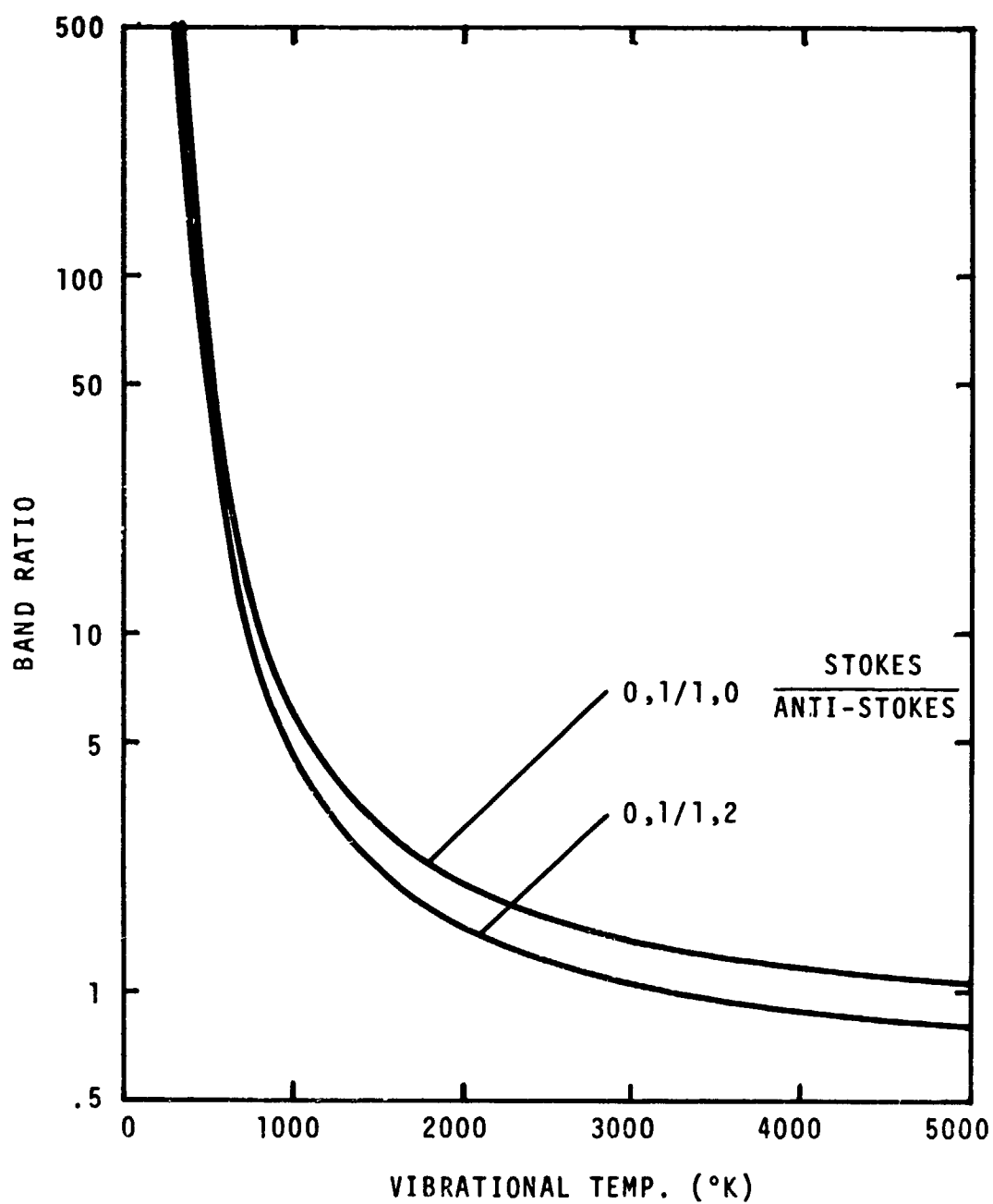


Figure 2. Various Raman Vibrational Band Ratios as a Function of Vibrational Temperature of Oxygen

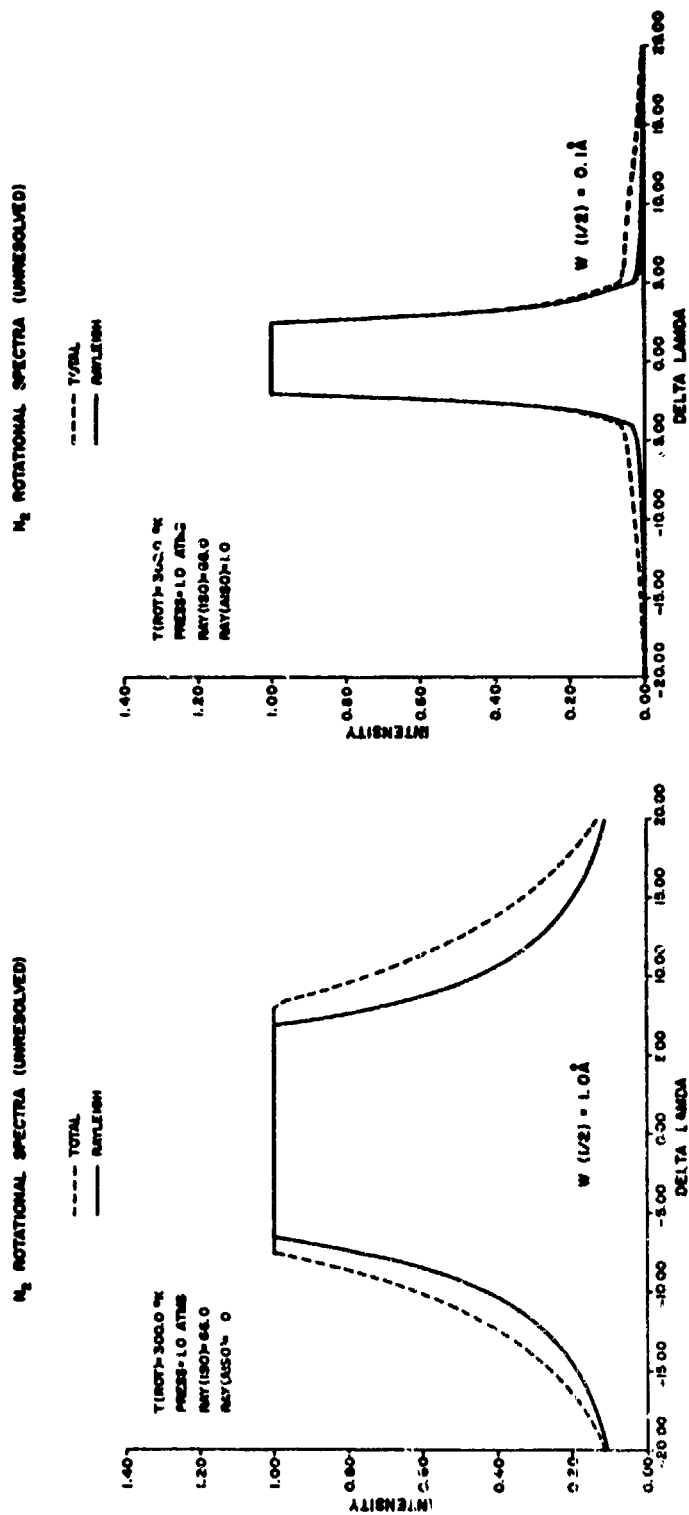


Figure 3. Unresolved Nitrogen Rotational Spectra for 1.0 and 0.1 Å Laser Line Half-Widths. (Spectrometer Slit Width is 50 μ)

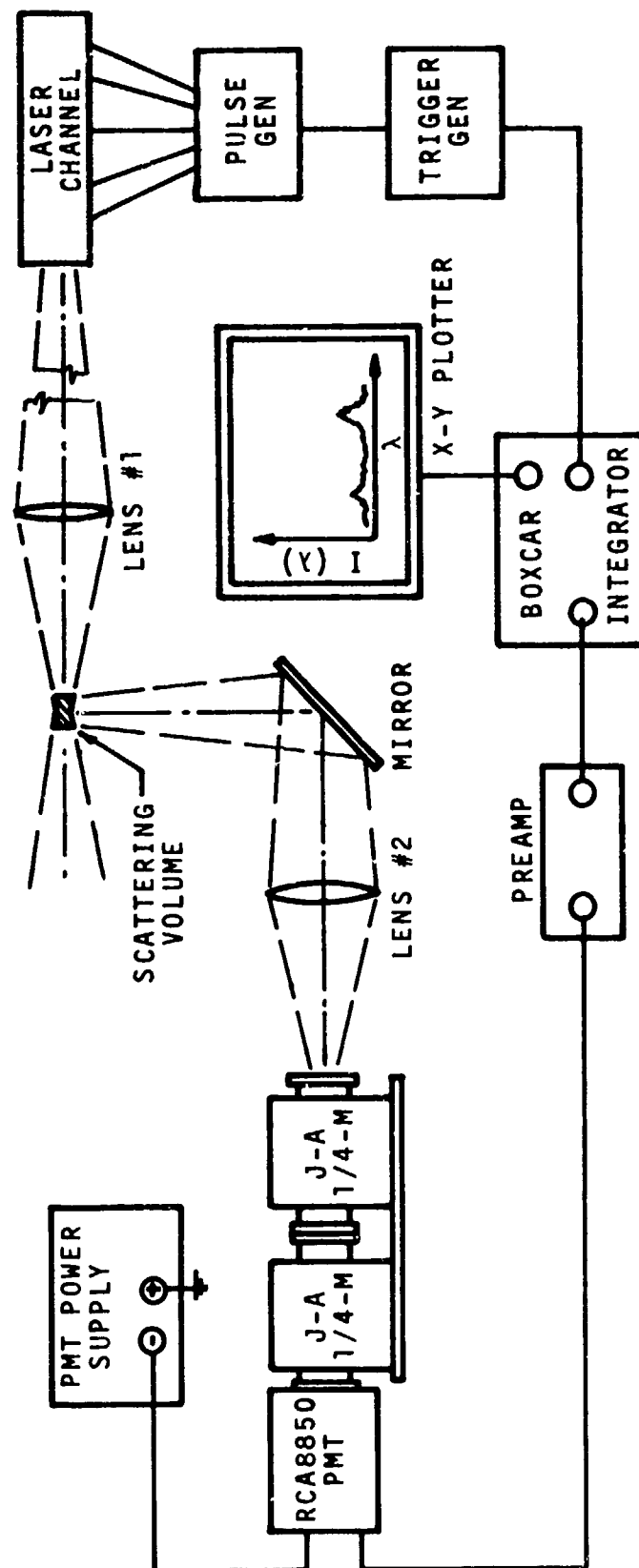


Figure 4. Block Diagram of LRS Experimental Setup Using Synchronous Detection of Pulsed Laser Output

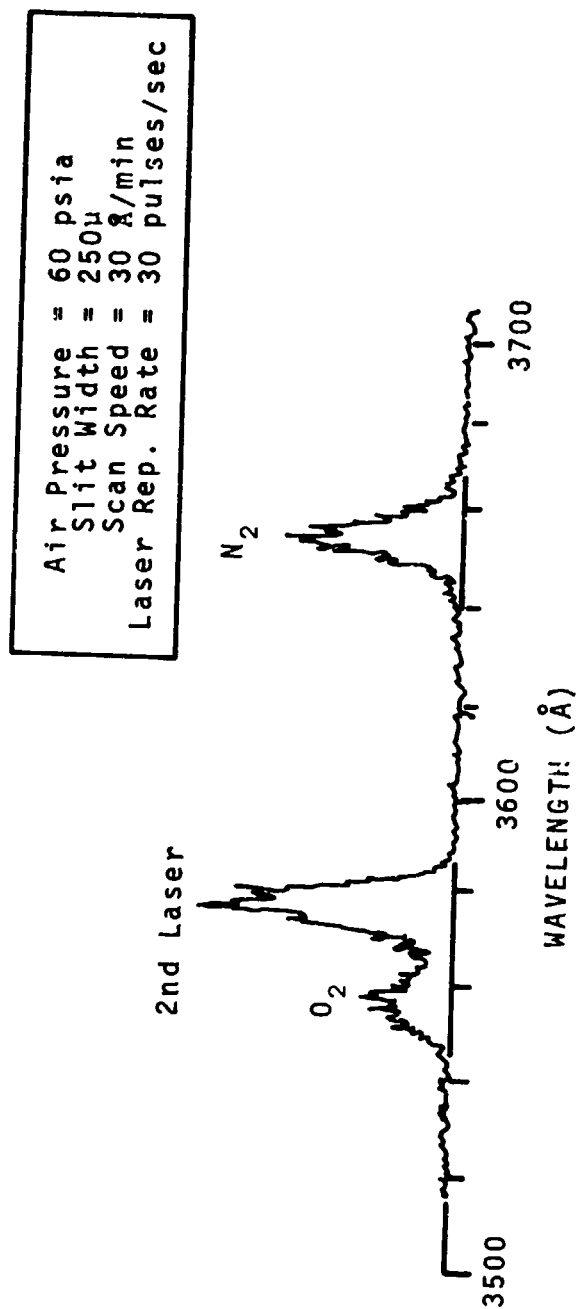


Figure 5. Raman Stokes Vibrational Spectra of Air at Room Temperature

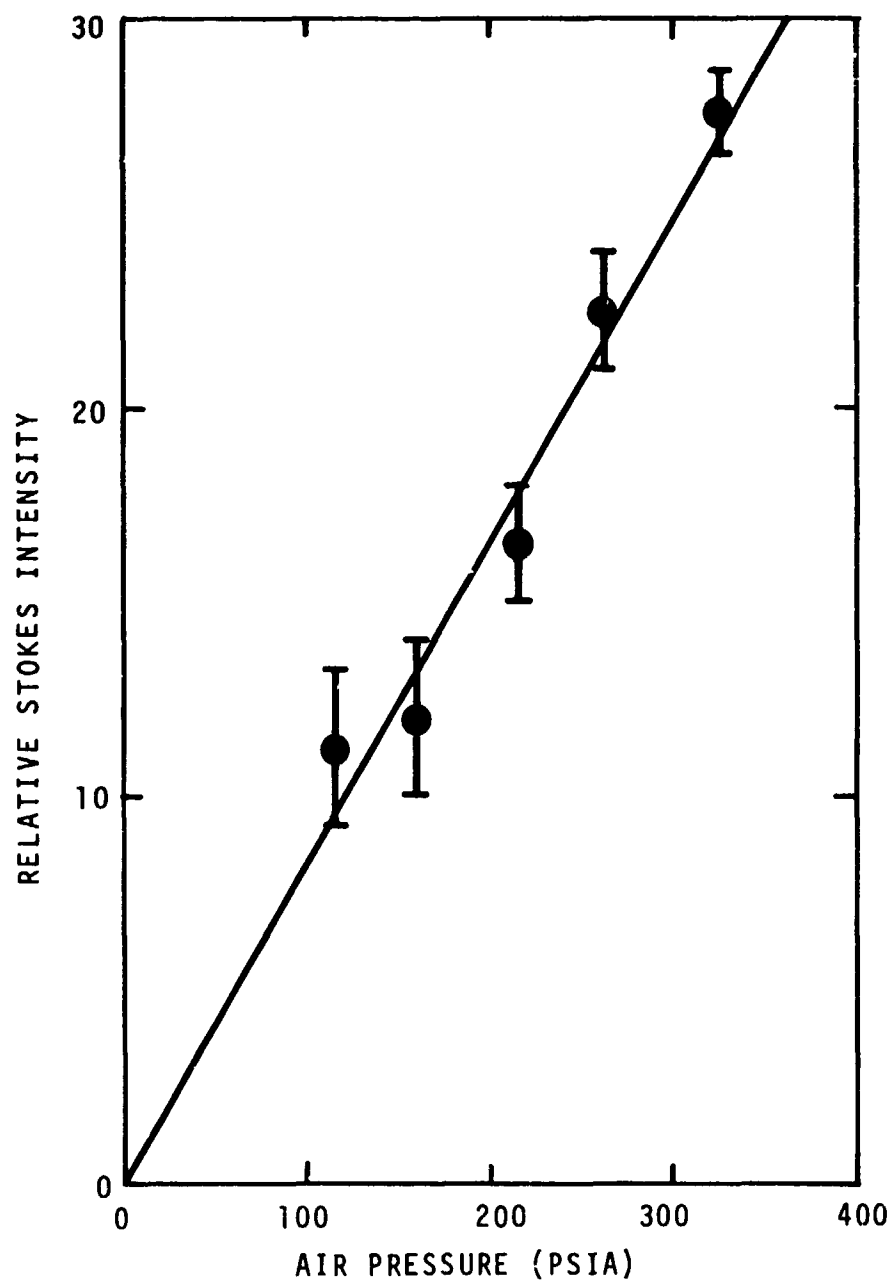


Figure 6. Raman Stokes Intensity of Nitrogen in Air at Room Temperature

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